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FINAL TECHNICAL REPORT

The Synthesis, Characterization and Formation Chemistry of Si-C-N-O-M Ceramic and Composite Powders.

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3. Product/Report Description

a. Publications

a.1.1 Yitbarek H. Mariam and Ke Feng, "Pyrolyzability of Preceramic Polymers," in Physical Properties of Polymers Handbook, James E. Mark, Ed., **AIP Press, 1996; Chap. 47**

a.1.2. Yitbarek H. Mariam and Ke Feng, "Preceramic Polymers" in Polymeric Materials Encyclopedia, Joseph C. Salamone, Ed.-in-Chief, **CRC Press, 1996, p. 7215**

b. 1. Published Proceedings.

b.1.1 K. P. W. Pemawansa, K. Feng and Y. H. Mariam, " Thermal and Oxidative Stability of SiNC Ceramics Derived from Poly(mathylvinyl)silyl Ethylenediamine" '**Polym. Mater.: Sci. Eng. 77, 487(1997).**

b.1.2. K. P. W. Pemawansa, K. Feng and Y. H. Mariam, " A Silicoboron Carbonitride Precursor Prepared by Chemical Modification of Poly(methylvinyl)silyl ethylenediamine" **Polym. Prepr., Am. Chem. Soc. Div. Polym. Chem. 38(2), 235(1997).**

b.2 Presentations/Conference.

b.2.1.

Yitbarek H. Mariam, " Studies in Reactivity"

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Sponsor: NSF 9th Annual Conference of National Alliance for Research Centers of Excellence (NARCE),

Location: El Paso,Texas, USA
Date: March,1997

b.2.2.

K. P. W. Pemawansa, K. Feng and Y. H. Mariam, "Thermal and Oxidative Stability of SiNC Ceramics Derived from Poly(mathylvinyl)silyl Ethylenediamine",

Sponsor: American Chemical Society National Meeting, Polym. Mater.: Sci. Eng. Div.,

Location: Las Vegas, NEVADA,

Date: September 1997

b.2.3.

K. P. W. Pemawansa, K. Feng and Y. H. Mariam, " A Silicoboron CarbonitridePrecursor Prepared by Chemical Modification of Poly(methylvinyl)silyl ethylenediamine",

Sponsor: American Chemical Society National Meeting, Div. Polym. Chem.

Location: Las Vegas, NEVADA,

Date: September 1997

BRIEF NARRATIVE

A. GENERAL PATTERN OF BEHAVIOR IN THE CONVERSION PROCESSES SiNC PRECURSORS. The understanding the chemical processes by which polymers are converted to ceramics has been a formidable challenge due to the complex nature of the polymer structures that serve as precursors, and due to the even more complex nature of the amorphous and intractable structures that are intermediates in the pyrolysis process. However, despite the overall similarities of the results of all the studies dealing with the structural evolution of different ceramic precursors reported in the literature, significant gaps still remain and a general pattern of behavior in the conversion process has not been established yet. It is not also apparent that a systematic study has been made to establish a general pattern for the formation chemistry of SiNC cramics.

One primary reason for why a general pattern has not been developed is probably the difficulty in assigning chemical shifts of silicon atoms that are in carbon, mixed carbon-nitrogen and mixed carbon-nitrogen-hydrogen environments such as SiN_2HC and SiN_3C tetrahedra. For example, in the transformation :

$$SiN_xC_yH_z \text{ ---> } [SiN_2HC/\ SiN_3C] \text{ ---> } SiN_4$$

$$(\text{where } x + y + z = 4 \text{ and } z \leq 1)$$

the assignment of Si sites corresponding to SiN_2HC and SiN_3C tetrahedra has been rather ambiguous. Clearly, the assignment of the $C\text{-}SiN_3$ signal by the Sigmund et al. and Brodie et al.groups (-21.5 vs -29 ppm, respectively) seem to be inconsistent with each other. In order to make a good accounting of the chemical events that take place during the bulk pyrolysis, a definitive identification of the intermediates that form during the structural evolution is necessary. Some literature reports have assigned signals with chemical shifts of about -20 ppm to both $SiH(C_{sp3})N_2$ and $Si(C_{sp3})N_3$. In another report a chemical shift of -22 ppm is assigned to SiC_2N_2 while $Si(C_{sp3})N_3$ is assigned to a chemical shift of 37 ppm. Clearly, some resolution of these discrepancies is needed.

There are also other gaps. It is also equally true that an attempt has not been made to at least qualitatively delineate the similarities and /or differences in the transformation of different precursors investigated by several groups. Also, to our knowledge, no extensive studies have been reported on the conversion processes of fully-characterized precursors that contain varying amounts of cyclic and acyclic moieties in the main chain. Moreover, despite the importance of knowing the complete molecular structure of the precursor for a full understanding of the conversion process, the complete structural characterization of ceramic precursors, to our knowledge, has been lacking, although this may have to do, in some cases at least, with the precursors not being amenable to such full characterization.

Studies on the effects of chain structure on the structural evolution and on a family of related systems to compare their structural evolution should help establish the general pattern of behavior of ceramic precursors. The advantage to these approaches is that not only the conversion process can best be understood in this way, but also it lends itself for the comparison of conversion processes of two or more structurally closely related systems to glean salient features in the miniralization process. It also lends itself for the evaluation of the importance of latent reactivity by comparing the conversion processes of precursors that have closely related chain structures but different latent reactivity.

The availability of fully-characterized precursors can be used not only for comparative studies of the trends in the transformation process, but also to address some of the trends identified by Wynne and Rice. Although Wynne and Rice had postulated that polymer structures containing rings or cages are expected to slow the kinetics of reversion reactions, and that branched-ring polymer structures give high ceramic yields (unlike linear polymers which give negligible ceramic yields because of reversion reactions and the generation of large, volatile molecules and cyclics), to what extent rings or cages and/or branched-ring structures improve the ceramic yield of a particular precursor can best be evaluated if the fraction of cyclic vs acyclic structures in a given precursor is determined a priori.

We, as one of the few groups, to our knowledge, who have investigated the conversion processes of cyclic SiNC precursors, have studied a class of polysilazanes of known microstructure, i.e., polymeric and/or oligomeric chains which have been fully characterized to determine the ratio of cyclic to acyclic disilazane structures in the main backbone. Specifically, we have investigated a family of precursors that can be represented as Si(ViCH3)N2 and Si(H)CH3)N2 systems, and the results of investigation of Si(ViCH3)N2 systems will be presented in plannned paper (under preparation), while another paper (in preparation) will focus on Si(H)CH3)N2 systems along with related ones. Thus, in these two reports, we will discuss our work on the conversion processes of a family of precursors that differ both in their microstructure and latent reactivity for the purposes of an ultimate first attempt to suggest that different precursors follow a general common pattern of organic-to-inorganic transformation, and also to demonstrate that the primary differences among different precursrs are:

(a) the cross-linking reactions they undergo,

(b) the ultimate composition of the final char.; and,

(c) the temperature at which a given intermediate forms.

More specifically, this report will focus on the assessment of the effect chain structure on the conversion process and/or formation chemistry along with the effects of thermal and oxidative treatments on the molecular environments (stability to thermal and oxidative treatments and structural effects that manifest due to such treatments), while the accompanying paper will explore the similarity in the transformation patter in a family of precursors. The results from both studies of these systems will be used in an attempt to establish a general pattern of behaviour for the structural evolution of the classes of precursors that have been converted to Si3N4.

B. THERMAL AND OXIDATIVE STABILITY OF SiNC CERAMICS. The effects of annealing (at 1500 0C) of samples pyrolysed at 900T have been investigated by IR, 13C, and

29Si NMR. Comparison of the spectral data on the annealed samples to that of the 900T sample clearly showed descernible changes which suggest phase separation and/or microcrystallization. X-ray diffraction data on the 900T and the annealed samples are also supportive of microcrystallization. The evidence indicated a partially crystalline material with amorphous halos. Both alpha and beta Si3N4 phases were observed with the alpha Si3N4 phase predominating , an observation that is consistent with the 29Si NMR data.

Results of oxidation in air and by $KMnO_4$. periodic acid and ozone suggest that at least in the case of periodic acid and ozone some oxidation seems to take place while there was no discernible oxidation from the use of the mild oxidizing agent $KMnO_4$ The results seem to suggest that most of the C_{sp2} phase is not oxidizable (and/or on the surface of the material). The spectral characteristics of the 900T sample and the sample annealed at 1500 0C showed significant differences for samples which were treated with periodate and ozone as oxidizing agents, the resultis indicating that the annealed sample is relatively more susceptible to oxidation.

C. MODIFICATION OF PMVSEDA WITH BORANE-DIMETHYL SULFIDE. Poly(methylvinyl)silylethylenediamine (PMVSEDA) prepared from methylvinyldichlorosilane (MVDS) to ethylene diamine (EDA) monomer feed-ratio of 1:2 was chemically modified using different amounts of borane-dimethyl sulfide (BDMS). From spectroscopic analysis of PMVSEDA and PMVSEDA modified with different amounts of BMDS, the general reactions involved in the modification (dehydrocoupling between NH and BH; reaction between $-Si-CH=CH_2$ and BH to give $-SiCH_2CH_2BH-$ or $SiCH(BH-)CH_2-$; Si-N bond breaking to generate Si-H functionality) and the likely structural units in the modified precursor gave a char yield (TGA to 1000 ^{0}C) of 83% which is 23% higher than that from the premodified oligomer with the increase coming mainly from a smaller weight loss between 450 ^{0}C and 700 ^{0}C . Elemental analyses showed the Si:N and Si:B ratios remained nearly constant after pyrolysis at 900 ^{0}C with the composition of boron being 20.1% in the ceramic char. IR and ^{29}SI NMR indicate B-N and SiN_3C are formed at the expence of SiN_4 tetrahedron which is consistent with the preference of B to bond with N since they have similar coordination characteristics. Although modification with boron leads to retention of more carbon in the ceramic char, ^{13}C NMR data do not indicate the presence of B_4C and the carbon phase appears to be carbidic/graphitic as in the ceramic char from the unmodified precursor (PMVSEDA) case.

D. MANUSCRIPT PREPARATION

Three manuscripts dealing with the results briefly outlined above are under preparation.